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Theory of Auger neutralization of positrons at metal surfaces

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Abstract : The transition rate in the process of positron neutralization *via* Auger mechanism during scattering from metal surfaces is studied. In this mechanism, a positron is neutralized by picking up an electron while another electron picks up enough energy to escape the potential barrier at the surface. A unitary transformation is introduced to the second quantized Hamiltonian The bound state is described by a state orthogonal to all conduction band states of the metal. The theory is applied to the case of a positron, capturing an electron from aluminum surface while an Auger electron is released. The neutralization rate is calculated as a function of distance from the surface. The transition rate for neutralization decays exponentially with distance from the surface. The general behavior is similar to the ion neutralization at metal surfaces

Keywords . Positron neutralization, positron-solid interaction, Auger neutralization.

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1. Introduction

One of the methods to study surfaces is by scattering ions. An ion beam of specific energy is directed onto the surface, and the product beam is analyzed. The product beam can contain ions, atoms, electrons or radiation. In low energy ion scattering (< 10 KeV), neutralized ions and electrons are produced [1–8]. During scattering, the ion can pick up an electron to be neutralized. Hagstrum [9] suggested that an ion moving near a metal surface can be neutralized by capturing an electron from the metal surface *via* a resonant tunneling or an Auger process if the atomic binding energy is larger than the surface work function. Similarly, a neutral atom can be ionized through the reverse charge transfer mechanism if the energy relationship is reversed. Experimental evidence of this have been observed in many experiments and it is well established now that neutralization and ionization play crucial roles in surface ion scattering [10] and ion-induced secondary electron emission [11,12]. Ion Neutralization Spectroscopy is used as an analytical technique to study surfaces [13–15]. Low energy ion scattering is a powerful tool to study the surface composition of solid surfaces [16]. This is important in heterogeneous catalysis, adhesion and segregation processes [17,18]. The advantage in low energy ion scattering is that due to the high neutralization probability, the information depth is reduced practically to the outermost atomic layers [19]. However, only charged scattered particles are detected in the experiments. This makes neutralization processes to strongly affect the signals taken, and a good understanding of the process of neutralization is of great importance for the understanding of the results. For structure analysis, the need for reliable theories is more pressing [20]. In secondary ion mass spectroscopy, it is necessary to know the final charge states of sputtered particles in order to draw conclusions about surface concentration of the sputtered species [21–23]. Another area where the understanding of this problem is of relevance, is in fusion research [24,25]. Here, one needs to know how many of the particles reflected from the wall of the reactor are charged, since only neutral particles can re-enter the plasma. This is in addition to the interest in the problem of neutralization in itself.

Ion neutralization at metal surfaces can take place through different mechanisms : resonance tunneling [2–4,9]; Auger neutralization [5–8]; surface plasmon excitation [1]; and radiative recombination. The response of the electronic system of the surface of the solid to a moving ion is highly dynamic such that approximations beyond normal first Born approximation are needed to explain experimental results [26]. In an earlier work, a theory was formulated to understand the process of ion neutralization *via* surface plasmon excitation [1]. In this theory, it was made use of a unitary transformation that would rotate the Fock space 'the physical space' by 2π into a new space which was called 'the ideal space'.

Carrying out the transformation, a new term 'the orthogonalization term' emerges in the matrix elements. This term appeared to be important for the process of surface plasmon-mediated neutralization. On a later work [2], the resonance tunneling mechanism for ion neutralization was considered using the same theory of implementing a unitary transformation which produced the orthogonalization term. This also showed importance of the correction in neutralization rate.

The orthogonalization is similar to that appearing in the theory of repulsive potential in atom-surface interaction due to electron kinetic energy gain. Of course, this is required as the decaying Bloch state of the metal electron orthogonalizes to the incident atomic state [27–29]. The orthogonalization comes out due to the use of pseudopotential with metallic states that are explicitly orthogonalizes to the atomic state. In this work, a calculation of the transition rate for Auger ion neutralization is carried out using a transformed Hamiltonian. This will give rise to an orthogonalization term that would give a more accurate value for the transition rate.

In this work, positron neutralization *via* the Auger mechanism is considered. The problem of positronium formation on metal surfaces has been considered extensively in the literature [30–33].

2. The ideal space Hamiltonian

The second-quantized Hamiltonian of our model representing the metal is given by

$$\hat{H} = \int dr \hat{\psi}^\dagger(r)\left[T(r) - |r-s|^{-1} + V_b(r)\right]\hat{\psi}(r) + \frac{1}{2}\int dr dr' \hat{\psi}^\dagger(r)\hat{\psi}^\dagger(r')V'_{el-el}(r,r')\hat{\psi}(r')\hat{\psi}(r). \quad (1)$$

In the Hamiltonian (1), $\hat{\psi}$ and $\hat{\psi}^\dagger$ are the electron annihilation and creation operators, $T(r)$ is the electron kinetic energy, $V_b(r)$ is the potential of the positive background, and $V'_{el-el}(r,r')$ is electron-electron interaction The jellium is assumed to occupy the half space $z \le 0$ where the surface is at $z = 0$ and $z > 0$ constitutes the exterior region. The electron position vector r in (1) may be either inside or outside the metal. Atomic units will be used throughout this paper.

The electron field operator will be expanded in terms of the complete orthonormal set of orbitals ϕ_k and corresponding annihilation operators $\hat{\psi}_k$ as

$$\hat{\psi}(r) = \sum \phi_k(r)\hat{\psi}_k. \quad (2)$$

The orbitals ϕ_k will be chosen to be eigenstates in a potential $V(z)$ which is constant inside and outside the metal with a step of height V_0 at the surface ($z = 0$), $V(z) = V_0\vartheta(z)$. Here, $V = F + W$ where F is the Fermi energy and W is the work function; and energies are measured from the bottom of the conduction band. The corresponding eigenfunctions ϕ_k are

$$\phi_k(r) = \frac{1}{k_v(V)^{1/2}}\left\{e^{ik\cdot r}\left[(k'_z + ik_z)\exp(ik'_z z) + (k'_z - ik_z)\exp(-ik'_z z)\right]\right\} \qquad z < 0$$

$$= \frac{1}{k_v(V)^{1/2}}\left\{2k_z e^{ik\cdot r}e^{-k_v z}\right\}, \qquad z > 0 \quad (3)$$

where V is the volume of the metal and k_z, k'_z and k_v are defined by

$$(k'_z)^2 = 2E'_k;\ k_z^2 = 2(V_0 - E'_k);\ k_v^2 = k_z^2 + (k'_z)^2 = 2V_0$$

with $E'_k = E_k - (1/2)^2 K$. Here, E_k is the eigenvalue of ϕ_k and K is the component of k parallel to the surface. Within the conduction band $E_k < F$, one has $0 < E'_k < E_k < F < V_0$, so that ϕ_k are oscillatory inside the metal and decay in the $+z$ direction outside.

3. Auger neutralization channel

The neutralized ion (the atom) will be described by a state orthogonal to all conduction band states by transforming to a new representation. The transformation which proved useful in earlier work [34] is unitary and takes the form

$$\hat{U} = e^{\left(\frac{\pi}{2}\right)\hat{F}};\ \hat{F} = \sum\left(\hat{A}^\dagger_\mu\hat{\psi}_\mu - \hat{\psi}^\dagger_\mu\hat{A}_\mu\right), \quad (4)$$

where $\hat{A}^\dagger_\mu = \int dr\,\phi_\mu(r-s)\hat{\psi}^\dagger(r)$. (5)

is the creation operator for an electron in a bound hydrogen orbital $\phi_\mu(r-s)$ centered on the proton (position s) and μ stands for the set of atomic quantum numbers. The operators $\hat{\psi}_\mu$ and $\hat{\psi}^\dagger_\mu$ operators are kinematically independent from the electron field operators $\hat{\psi}$ and $\hat{\psi}^\dagger$

and anticommute with them. The transformed Hamiltonian will then act on the physical state which takes the form

$$[....) = \hat{U}^{-1}|.....\rangle$$

where $|.....\rangle$ is any standard Fock state created by acting on the vacuum state by the electron creation operator.

The transformed Hamiltonian can be evaluated using the transformation results of the electron field operators $\hat{\psi}(r)$ which transform as follows [34] :

$$\hat{U}\hat{\psi}(\bar{r})\hat{U} = \hat{\psi}(\bar{r}) - \int d\bar{r}'\Delta(\bar{r}-\bar{s},\bar{r}-\bar{s})\hat{\psi}(\bar{r}') + \sum \phi_\mu(r-s)\hat{\psi}_\mu, \quad (6)$$

where $\Delta(r-s,r'-s)$ is the bound state kernel

$$\Delta(r-s,r'-s) = \sum \phi_\mu(r-s)\phi_\mu^*(r'-s). \quad (7)$$

The Auger neutralization channel can only come from transforming the fourth term in the Hamiltonian,

$$\int drdr'\hat{\psi}^\dagger(r)\hat{\psi}^\dagger(r')V'_{el-el}(r,r')\hat{\psi}(r')\hat{\psi}(r). \quad (8)$$

The transformed term takes the form

$$\int drdr'\hat{U}^{-1}\hat{\psi}^\dagger(r)\hat{\psi}^\dagger(r')V'_{el-el}(r,r')\hat{\psi}(r')\hat{\psi}(r)\hat{U}. \quad (9)$$

This can be manipulated by inserting an identity operator $\hat{U}\hat{U}^{-1}$ in between the operators in the following way

$$\int drdr'\hat{U}^{-1}\hat{\psi}^\dagger(r)\hat{U}\hat{U}^{-1}\hat{\psi}^\dagger(r')\hat{U} \times V'_{el-el}(r,r')\hat{U}^{-1}\hat{\psi}(r')\hat{U}\hat{U}^{-1}\hat{\psi}(r)\hat{U}. \quad (10)$$

This transformation can now be carried out using eq. (6) to get eighty one terms. This will result from multiplying three terms by three terms and the result by another three terms and then finally by three new terms. All two-electron scattering channels that might occur will be represented in those eighty one terms. The terms of interest here that are for the neutralization *via* Auger process are

$$\hat{T}_1 = \sum_\mu \int drdr'\phi_\mu^*(r-s)\hat{\psi}^\dagger(r)\hat{\psi}_\mu^\dagger V'_{el-el}\hat{\psi}(r')\hat{\psi}(r) \quad (11)$$

$$\hat{T}_2 = \sum \int drdr'dr''\phi_\mu^*(r'-s)\Delta(r-s,r''-s) \times \hat{\psi}^\dagger(r'')\hat{\psi}_\mu^\dagger V'_{el-el}\hat{\psi}(r')\hat{\psi}(r) \quad (12)$$

The physical interpretation of these two terms is clear. The first term $\hat{T}_1$ corresponds to an Auger process in which the annihilation field operators $\hat{\psi}(r')\hat{\psi}(r)$ annihilate two electrons at r' and r and as a result, the creation operators $\hat{\psi}^\dagger(r'')\hat{\psi}_\mu^\dagger$ create an Auger electron and an electron bounded to the ion. The second term $\hat{T}_2$ corresponds to the same process as the first, except that it involves the bound state kernel (Δ is the kernel of the integral projection operator onto the bound atomic states). This guarantees orthogonalization of the metal orbitals to all bound atomic orbitals. Therefore, no spurious contributions representing Auger atomic bound-bound electrons enter into the matrix elements representing the scattering studied.

Using the expansion of the field operators $\hat{\psi}(r)$ for the electrons in terms of wave functions and annihilation operators as in (2), one finds the expression for the perturbation $\hat{H}_{int}$ leading to the Auger neutralization

$$\hat{H}_{int} = \sum (\mu,k_1|H_{int}|k_2,k_3)\hat{\psi}_{k_1}^\dagger\hat{\psi}_\mu^\dagger\hat{\psi}_{k_2}\hat{\psi}_{k_3}, \quad (13)$$

where the matrix elements are given by

$$(\mu,k_1|H_{int}|k_2,k_3) = \int drdr'\phi_\mu^*(r-s)\phi_{k_1}^*(r) \times V_{ee}\phi_{k_2}(r')\phi_{k_3}(r) - \int drdr'dr''\phi_\mu^*(r'-s) \times \Delta^*(r-s,r''-s)\phi_{k_1}^*(r)V_{ee}\phi_{k_2}(r')\phi_{k_3}(r). \quad (14)$$

The matrix element in (13) is a form of Born approximation to exact T-matrix element for the process being considered. However, it is a better approximation due to the influence of the orthogonalization term (the second term). This term was found to be important in neutralization *via* resonance tunneling [2] and surface plasmon excitation [1].

4. The matrix element

Here, the calculations will be carried out for the simplest case in which the final atomic state is the ground ($1s$) state of positronium. The final positronium state will take a form based on the work of Gadzuk [35] who considered the quantum mechanics of atom-solid surface interaction in a general way. Let us illustrate the situation by considering positronium as a pair of a positron and an electron. Into the positronium system, we introduce the relative coordinates r and the coordinates of the center of mass R as follows :

$$r = r_+ - r_-,$$

$$R = (r_+ + r_-)/2.$$

The wave function of the $1s$ state of positronium can be presented using the above coordinates as

$$\phi_{1s}(r-r) = e^{-|r-s|/2}e^{iK\cdot s}. \quad (15)$$

Note that this will make our matrix element unreliable for $s \leq 1$. The potential V_{el-el} in (1) will be taken to be the screened Coulomb interaction

$$V_{el-el} = \frac{e^{-\lambda|r-s|}}{|r-s|}$$

where λ is the inverse screening length. The matrix element will be evaluated by substituting $\phi_k(r)$ for the surface electron state and $\phi_v^*(r-s)$ for the bound electron state in (15). The first term will be the direct term, while the other one is a series over all bound states of the positronium.

The transition rate P of the scattering being considered here, is not simple since the scatterer (the metal surface) is a many body system. The Auger neutralization process can be indicated schematically by

$$\text{medium} \rightarrow \text{medium}' + \text{positronium} + \text{Auger electron}.$$

The medium stands for the many-body system of electrons, and the prime indicates a different state after scattering. Using the theory of reactive scattering by large systems such as surfaces [35], the transition rate takes the form

$$P = 2\pi \sum \omega_i \left|\left(f\left|H_{in}\right|i\right)^2\right| \delta(E_i - E_f), \tag{16}$$

where the sum is over all the final states, and ω_i is a statistical weight for the average over the ensemble of the initial medium states. The exact many body transition operator is denoted by H_{in}. The final positronium state has been taken to be the $1s$ state. The prime on the summation sign indicates the restriction that the k sum is over the interior of the filled Fermi sea only.

The matrix elements M for the neutralization channel are now taken from the actual evaluations. This gives for the transition rate, the simple form

$$P = 2\pi \sum |M|^2 \delta(E_i - E_f). \tag{17}$$

Changing the sum into an integral, we get

$$P = \frac{2\pi 2V}{(2\pi)^3} \int dk |M|^2 \delta(E_i - E_f). \tag{18}$$

Here, $\varepsilon_i = \frac{1}{2}k_2^2 + \frac{1}{2}k_3^2$ is the metal electrons energy and $\varepsilon_f = E(1s) + \frac{1}{2}k_1^2$ is the atomic and Auger electron energy, V is the volume and 2 is for the double spin of the electron.

5. Results and Conclusions

To apply the theory developed, here we will assume the scattering system as

$$e^+ + e^- \text{ (Al metal)} \rightarrow Ps(1s) + e^- \text{ (Auger)}. \tag{19}$$

The aluminum is chosen because it satisfies best the assumptions made in the theory. Firstly, it can be well-approximated by a jellium model. Secondly, its Fermi surface is very close to the free electron surface for a face centered cubic monatomic Bravais lattice with three conduction electrons per atom. Thirdly, the existence of experimental work on this system for the comparable case of ion neutralization (proton scattered from aluminum surface) [8], in addition to the theoretical work where other mechanisms of neutralization are assumed [1,2]. To authors' knowledge, no experimental results have been published for this mechanism. The parameters used for aluminum are : 0.9261 for the Fermi wave vector k, 0.5862 for the surface potential V. Eq. (18) is used to calculate the transition rate P as a function of the distance s of the positron from the surface. The integration over k is calculated numerically. All other calculations are done analytically using the inverse Fourier transform integrals and making use of the calculus of residues [1,2].

Figure 1 shows the neutralization rate P as a function of the distance s from the surface. From the figure, it is clearly evident that the transition rate decays exponentially with distance from the surface. This behaviour is expected from

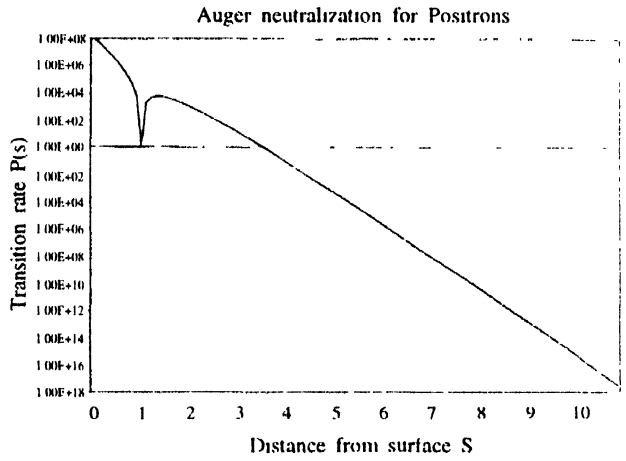

Figure 1. Transition rate $P(s)$ *via* Auger mechanism as a function of the distance s from the surface for positron scattering from aluminum surface

the exponential nature of the positronium and metal wavefunction tails in the region $z > 0$, and from the exponential dependence on the screening length in the form of the screened Coulomb interaction potential V_{el-el}. A simple exponential form for the ion neutralization transition rate was in fact suggested by Hagstrum [9].

From the figure, it is observed that the transition rate attains a local maximum value at $s = 1.3$ and a local minimum at $s = 1$ forming a dip in the exponential curve around $s = 1$. This can be explained by considering the positron at small distances from the surface. The general behaviour is similar to the ion neutralization at metal surface. At small distances, the transition rate is greatly affected in the important region for neutralization namely, small distances from the surface. In this region, the repulsive potential due to the positive background of the metal has large values. This decreases the total potential (attractive

and repulsive) and consequently, the transition rate. The effect of lowering the transition rate is accomplished in our theory by the orthogonalization term in the matrix element which is subtracted from the original matrix element. The attractive potential (positron charge with the electron density) also increases at small distances from the surface. These two effects add up to a potential that give rise to the turnover region. The incident positron will penetrate into the turnover region when the electron density on the surface is such that the rate of increase of attractive potential is greater than that of the repulsive potential.

From the results demonstrated on the graph, it is concluded that the Auger mechanism for positron neutralization during scattering from metal surfaces is of high probability, especially at small distances from the surface; and the transition rate decreases quickly at large distances from the surface. The distance $s = 1$ is of special interest as the transition rate at this distance behaves differently and probably deserves more detailed work. In future, work on other possible mechanisms, namely, resonance tunneling and surface plasmon will be considered. This will enable to compare between the transition rates for the different mechanisms.

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